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Physical and optical properties of dysprosium ion doped strontium borate glasses

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ABSTRACT

The effect of dysprosium ion (Dy^{3+}) on the optical absorption and band gap energy of strontium borate glass systems prepared by melt quenching technique have been reported. The results show that the broad absorption edge of doped glasses shifts back and forth as a function of Dy_2O_3 concentrations. The intensities of five prominent and two weak optical transitions change accordingly with Dy_2O_3 concentrations. The defect centres are induced with the presence of Dy^{3+} ions in glass samples. This attributes to the intra-configurational (*f–f*) transitions of Dy^{3+} ions in glass network. In addition, the decreasing trend of optical band gap energy and Urbach energy can be related to defect centres created by Dy^{3+} ions. The FTIR study reveals the presence of BO_3, BO_4 vibration groups and the bending of B–O–B units. The asymmetric stretching of BO_3 and BO_4 was apparent at higher Dy_2O_3 concentrations. More tetrahedral BO_4 units were formed by increasing Dy_2O_3 concentrations. The dependency of Dy_2O_3 concentrations on the optical properties is further discussed with other important physical properties.

1. Introduction

The properties of glasses are well studied by many researchers due to their easy preparation, good strength, high transparency, and excellent isotropic materials. These studies include the exploration of the local environment of doping ion (rare earth and transition metal) and modifier incorporated to the host materials such as borate, silicate, phosphate or germanium through Fourier transform infrared spectroscopy [1], nuclear magnetic resonance [2], luminescent spectroscopy [3–5], and electron spin resonance analyses [6].

Borate glass is commonly known for its high thermal stability, low melting point, different coordination numbers and good solubility of rare earth ions [7]. However, pure borate glass is hygroscopic and sensitive to its surrounding atmosphere. The glass easily becomes unstable due to its ability of absorbing water especially in moisturised environment. Physical and optical properties of glasses can be enhanced by the addition of modifiers such as alkaline and alkaline earth ions. For instance, alkali and alkaline earth ions based borates have been used in various applications such as vacuum ultraviolet (VUV) optics, radiation dosimetry and solar energy converters [8,9].

Various studies have been conducted to explore the physical and optical properties of borate glasses doped with different compositions of rare earth [10–15]. Rajesh and his colleagues have reported the structural and spectroscopic investigations of strontium lithium bismuth borate glasses doped with Pr^{3+} and Nd^{3+} [10], Dy^{3+} [11], Sm^{3+} [12], and Er^{3+} [13]. They explained the reduction of emission intensity of Dy^{3+} ion as a result of energy transfer through cross relaxation and resonance energy transfer at doped concentrations beyond 0.5 mol%. Gedam et al. have reported the effect of Nd_2O_3 on conductivity and optical properties of lithium borate glasses for scintillating applications [14]. Tawfik et al. have studied physical properties of Sm^{3+} ion doped borochromate glass systems and have confirmed that Sm_2O_3 and Cr_2O_3 exhibited a minor effect on the boron network [15].

In this work, we intend to study the effect of Dy^{3+} ion on the optical properties of strontium borate glasses and calculate the optical band gap energy. According to the best knowledge of authors, no one has studied the strontium borate glasses with varying concentrations of Dy^{3+} ion. Bearing in mind these considerations, the present study is focused on the physical properties, FTIR analyses, optical absorption and optical band gap energy.

2. Experimental

The strontium borate glass samples from the series of $(66.67-x/2)\ B_2O_3$–$(33.33-x/2)$ SrO: $x\ Dy_2O_3$ (where $x=0$, 0.15, 0.25, 0.5, 0.75 and 1.0 mol%) were prepared by conventional melt quenching method as listed in Table 1. The glass samples were referred as BSD, and the following number was the molar percentage of Dy_2O_3 that was incorporated to strontium borate glass.

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Exact amount of analytical grades of boric oxide (B_2O_3), strontium carbonate ($SrCO_3$) and dysprosium oxide (Dy_2O_3) were mixed in an alumina crucible and melted at 1200 °C for approximately 15–30 min based on their compositions. The molten materials were stirred frequently and poured onto a stainless steel plate, and pressed quickly with another plate to reduce thermal strain.

The physical parameters such as density, refractive index, molar volume, molar refractivity, ion concentration, polaron radius, inter-nuclear distance, dielectric constant, reflection loss, electronic polarizability, optical basicity and metallization criterion were measured and calculated [16–20]. The densities were measured by using Archimedes principle. The refractive index measurements were carried out using Shimadzu 3101 UV–vis–NIR spectrophotometer and data fit software version 9.059 in the wavelength region 200–800 nm [17]. The absorption spectra were also recorded using the same spectrophotometer with the same wavelength region. The infrared spectra were obtained using FTIR spectroscopy. Potassium bromide (KBr) pellet method was employed and the spectra were recorded using Perkin-Elmer Spectrum One FT-IR spectrometer in the wave number of range 400–2000 cm^{-1}. All measurements were conducted at the room temperature.

3. Results and discussion

3.1. Physical properties

Table 2 lists the physical parameters such as density, molar volume, average molecular weight, refractive index, molar refractivity, ion concentration, polaron radius, inter-nuclear distance, field strength, electronic polarizability, optical basicity, metallization criterion, dielectric constant and reflection loss of the prepared glass samples.

The density for BSD glasses increase with the increasing of Dy_2O_3 concentrations (Table 2). The same trend is also seen for average molecular weight of BSD glasses. This is because of higher molecular mass of Dy_2O_3 compared to SrO and B_2O_3. In addition, an increase in densities can be related to a change in the geometrical and coordination configuration, structural softening and the dimension of interstitial spaces of the glass [21,22]. The molar volume of BSD glasses increase by the addition of Dy_2O_3 up to 0.5 mol%. Beyond this concentration, the observed molar volume starts to decrease at 1.0 mol% Dy_2O_3 with 26.78 cm^3 mol^{-1}. This result is in good agreement with work of Saddeek about lead sodium borate glass [22]. This reduction may be attributed to the creation of non-bridging oxygens and breaking of covalent bond between boron and oxygen atom at a concentration of 0.5 mol% Dy_2O_3.

Furthermore, the polaron radius listed in Table 2 decreases with increasing of Dy_2O_3 concentration. This could be due to an increase in N for Dy^{3+} ion. As a consequence, one could expect a high field strength around Dy^{3+} ions. The observed decrease in the inter-nuclear distance with an increase of Dy_2O_3 concentration eventually leads to a more compact boron network of BSD glass systems.

According to Eraiah [23], the refractive index and molar refraction have a closed relationship with polarizability properties. As the Dy_2O_3 concentration was increased up to 0.25 mol%, the refractive index and molar refraction decreased. Beyond 0.50 mol% Dy_2O_3, the observed refractive index and molar refraction increase. As expected, the electronic polarizability reduces with the increasing of Dy_2O_3 concentration since it is inversely proportional to the number of oxide ion $N_{O^{2-}}$. However, one can notice a slight increase in the electronic polarizability of BSD50 and BSD75 glass samples, which is resulting from the variables of molar volume V_M and $N_{O^{2-}}$. The high polarizability can be explained with the formation of non-bridging oxygens in BSD glasses. Thus, the bond energies of Dy^{3+} ions reduce as the number of ionic bonds are higher than the number of covalent bonds in BSD glasses.

The optical basicity serves in the first approximation to estimate the ability of oxygen in donating negative charge to show the degree of covalency for glassy samples [15]. From Table 2, the optical basicity of glasses becomes higher with the increasing Dy_2O_3 concentration. However, there is some decrement of optical basicity for BSD25 and BSD100 glasses. This could be due to the

Table 1
Composition of the Dy_2O_3 doped strontium borate glass samples.

Glass notation	Concentration (mol%)		
	B_2O_3	SrO	Dy_2O_3
BSD0	66.67	33.33	0.00
BSD15	66.59	33.26	0.15
BSD25	66.54	33.21	0.25
BSD50	66.42	33.08	0.50
BSD75	66.29	32.96	0.75
BSD100	66.17	32.83	1.00

Table 2
Physical properties of BSD glass samples.

Properties	Samples					
	BSD0	BSD15	BSD25	BSD50	BSD75	BSD100
Density, ρ (g cm^{-3}) ($\pm$0.04)	2.96	2.95	2.96	2.98	3.02	3.13
Average molecular weight, $\overline{M}$ (g)	80.95	81.38	81.67	82.38	83.10	83.81
Molar volume, V_M (cm^3) ($\pm$0.01)	27.35	27.59	27.59	27.64	27.52	26.78
Refractive index, n ($\pm$0.01)	1.98	2.00	1.91	1.97	2.00	1.99
Molar refractivity, R_M ($\pm$0.02) [18,19]	13.49	13.79	12.94	13.54	13.76	13.30
Ion concentration, N ($\times 10^{20}$ ions cm^{-3}) ($\pm$0.01) [20]	–	0.33	0.55	1.09	1.64	2.25
Polaron radius, r_p (Å) ($\pm$0.01) [16]	–	12.56	10.60	8.44	7.36	6.63
Inter-nuclear distance, r_i (Å) ($\pm$0.01) [16]	–	31.18	26.30	20.93	18.27	16.44
Field strength, F ($\times 10^{15}$ cm^{-2}) ($\pm$0.01) [20]	–	0.19	0.27	0.42	0.55	0.68
Electronic polarizability, $\alpha_{O^{2-}}$ (cm^3) ($\pm$0.05) [19]	2.05	2.10	1.95	2.05	2.09	2.01
Optical basicity, Λ ($\pm$0.02) [19]	0.86	0.87	0.81	0.86	0.87	0.84
Metallization criterion, M ($\pm$0.02) [19]	0.51	0.50	0.53	0.51	0.50	0.50
Dielectric constant, ε ($\pm$0.01) [16]	3.92	4.00	3.65	3.88	4.00	3.96
Reflection loss, R(%) ($\pm$0.02)	10.81	11.11	9.78	10.67	11.11	10.96